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Influence of the ice growth rate on the incorporation of gaseous HCl

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Abstract. Ice crystals were grown in the laboratory at -15°C , at different growth rates and in the presence of a partial pressure of HCl of 1.63×10^{-3} Pa, to test whether the ice growth rate influences the amount of HCl taken up, X_{HCl} , as predicted by the ice growth mechanism of Domine and Thibert (1996). The plot of HCl concentration in ice as a function of growth rate has the aspect predicted by that mechanism: X_{HCl} decreases with increasing growth rate, from a value that depends on thermodynamic equilibrium to a value that depends only on kinetic factors. The height of the growth steps of the ice crystals is determined to be about 150 nm from these experiments. We discuss that the application of these laboratory experiments to cloud ice crystals and to snow metamorphism is not quantitatively possible at this stage, because the physical variables that determine crystal growth in nature, and in particular the step height, are not known. Qualitative applications are attempted for HCl and HNO_3 incorporation in cloud ice and snowpack crystals.

1 Introduction

The understanding of snow composition is crucial for numerous scientific fields such as ice core inversions (Domine et al., 1995; Legrand and Mayewski, 1997), air-snow interactions (Domine and Shepson, 2002), hydrology (Tranter et al., 1986; Cragin et al., 1993; Domine and Thibert, 1995) and ecology (Crittenden, 1998). Snow on the ground undergoes metamorphism, a set of physical processes which includes sublimation-condensation cycles that lead to changes in the size and shapes of snow crystals (Colbeck, 1982; Domine et al., 2003). These changes are caused mostly by the thermal gradient in the snow, that lead to water vapor fluxes, which in turn entrain gases dissolved in the crystalline lat-

tice of the snow crystals or adsorbed on their surface. Many studies monitoring the composition of the snow after deposition have observed significant changes in the concentration of gases contained in the snow phase (see for example Hutterli et al. (2002) and Perrier et al. (2002) for HCHO; Jacobi et al. (2002) for HCHO and H_2O_2 ; Domine et al. (1995) for HCl; Rothlisberger et al. (2002) for HNO_3). Many processes can be invoked to explain those changes: solid state diffusion out of snow crystals as suggested by Perrier et al. (2002) for HCHO, release during metamorphism as suggested by Nakamura et al. (2000) in the case of HNO_3 , photolysis as suggested by Jones et al. (2001) for HNO_3 , and the release of desorbed species because of the decrease in the specific surface area of snow during metamorphism, as suggested theoretically for acetone by Domine et al. (2002) and for acetaldehyde from measurements by Houdier et al. (2002).

The purpose of this work is to contribute to the understanding of the role of metamorphism in the change in composition of snow crystals. The data obtained are also applicable to the composition of ice crystals in clouds. The mole fraction of gases dissolved in ice will be the result of kinetic and thermodynamic processes. Domine and Thibert (1996) have proposed a physical mechanism to predict the concentration of a dissolved gas as a function of the growth rate of the ice crystal and of the intrinsic properties of the gas. At very fast growth rates, the gas mole fraction in ice, X_{gas} , is predicted by condensation kinetics, and is then X_{kin} :

$$X_{\text{kin}} = \frac{P_{\text{gas}} \gamma_{\text{gas}}}{P_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \sqrt{\frac{M_{\text{H}_2\text{O}}}{M_{\text{gas}}}} \quad (1)$$

where P is the partial pressure, γ is the uptake coefficient on the ice surface, M is the molar mass, and the subscripts H_2O and gas pertain to water and the dissolved gas, respectively. Domine and Thibert (1996) actually used α , the mass accommodation coefficient, rather than γ . However, both in the atmosphere and in many laboratory setups, the observed

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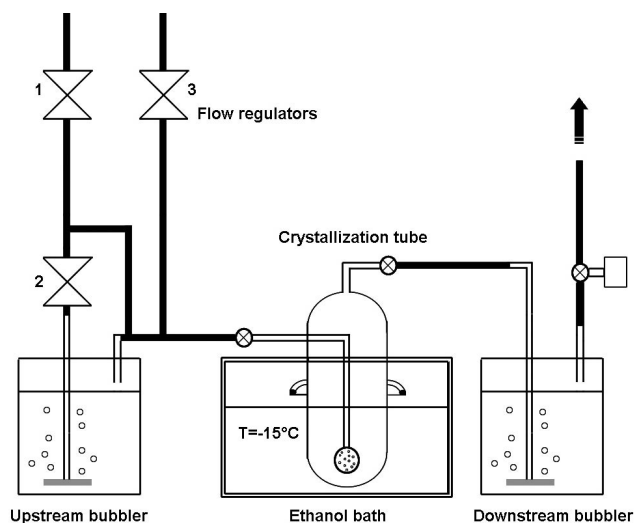


Fig. 1. Experimental system used to study the incorporation of HCl in growing ice crystals. Three flow regulators and a bubbler filled with ultra pure water are used to set the partial pressures of HCl and H₂O diluted in N₂ at atmospheric pressure. The crystallization tube is partly immersed in an ethanol bath at -15°C . A second bubbler is sometimes added downstream of the cold bath to trap HCl.

uptake results from numerous factors that include the surface accommodation itself, but also limitations due to diffusion in the gas phase, desorption and solid state diffusion (Hanson, 1997; Ammann et al., 2003), so that it is more appropriate to use the variable γ , that is not influenced just by surface processes, and that represents a better description of observations in many systems.

At very slow growth rates, X_{gas} is determined by the thermodynamics of the solid solution of the gas in ice, that predict $X_{eq} = f(T, P_{gas})$, where T is temperature and X_{eq} is the mole fraction of the gas dissolved in ice at thermodynamic equilibrium. This is known for HCl and HNO₃ (Thibert and Domine, 1997 and 1998). For HCl, this relationship is:

$$X_{\text{HCl}} = 6.1310^{-10} e^{\left(\frac{2806.5}{T}\right)} (P_{\text{HCl}})^{\frac{1}{2.73}} \quad (2)$$

with T in Kelvin and P_{HCl} in Pa.

In many cases, however, both kinetic and thermodynamic factors contribute to X_{gas} . Domine and Thibert (1996) mentioned that under atmospheric conditions, the growth of ice crystals is a discontinuous process that takes place by the propagation of new growth steps nucleating at crystal edges. Each new step, of thickness h , is then formed with a composition X_{kin} determined by (1). Since this is out of equilibrium with the atmosphere, solid state diffusion of the gas in the ice lattice will take place to drive the composition towards X_{eq} . Equilibration can proceed during a duration τ , after which a new ice layer is deposited, isolating the lower layer from the atmosphere and blocking diffusion from the gas phase. The

resulting X_{gas} value is then given by :

$$X_{gas} = X_{kin} + \frac{(X_{eq} - X_{kin})}{h} \int_0^h \text{erfc}\left(x/2\sqrt{D_{gas}\tau}\right) dx \quad (3)$$

where D_{gas} is the diffusion coefficient of the gas in ice and erfc is the complementary error function. In the case of HCl, under most tropospheric conditions $X_{kin} < X_{eq}$, and Eq. (3) thus predicts that at slow growth rates, X_{HCl} will be higher than at fast growth rates. Thus, in a snowpack undergoing intense metamorphism driven by a strong temperature gradient leading to fast crystal growth (Domine et al., 2003), X_{HCl} of snow should be lower than in a snowpack subjected to a low temperature gradient, where crystal growth will be slow. In clouds, where crystal growth is almost always faster than in the snowpack, this predicts that HCl concentration will be mostly determined by kinetic factors, as observed by Domine and Thibert (1996).

In this paper, we describe laboratory experiments that test semi-quantitatively the model of Domine and Thibert. A fully quantitative test would require the monitoring of the step thickness and also the understanding of the various factors that control variations in the sticking coefficient of gases on solid surfaces, such as the state and defect density of the surface and the growth rate of the solid (Henderson, 2002). This would involve extensive instrumentation in surface science and solid state physics, and is well beyond the scope of the paper, whose objective is limited to testing that the growth rate of an ice crystal does indeed condition the incorporation of dopants. We thus grew ice crystals at several growth rates in the presence of a fixed P_{HCl} . HCl was chosen because its solid solution with ice has been extensively studied, and its diffusion coefficient in ice is known (Thibert and Domine, 1997). From the data, we also attempt to determine h , the height of the growth steps in our experimental system.

2 Experimental methods

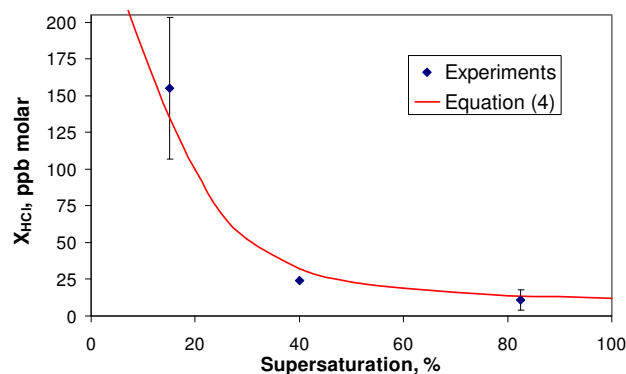
Gas mixtures of H₂O and HCl diluted in N₂ were flowed into a crystallization tube as shown in Fig. 1. The upstream bubbler was filled with ultra pure water (resistivity $>18 \text{ M}\Omega \text{ cm}$), placed in a dewar thermostated at 0°C , and the N₂ flow through that bubbler was adjusted to obtain the desired supersaturation in the crystallization tube, and this controlled the growth rate. Supersaturation values of the incoming mixture were determined from the data of Marti and Mauersberger (1993) and from the temperature of the stirred ethanol bath, regulated within 0.01°C . The error in the supersaturation was determined by the error in the bath temperature and by the precision of the flow regulators (4%), and was less than 10%. HCl came from two commercial mixtures (Air Liquide) of HCl in N₂ of molar concentrations 9.9 and 45.6 ppm. These concentrations were verified by flowing known amounts of mixture in the downstream bubbler,

Table 1. Experimental conditions and results for the incorporation of HCl in ice as a function of the supersaturation of the gas mixture in H₂O relative to ice at -15°C .

Experiment duration h	Supersaturation %	$P_{\text{H}_2\text{O}}$ Pa	P_{HCl} Pa	Number of experiments	Average $[\text{Cl}^-]$ (blank subtracted) ppb molar	Standard deviation ppb molar
64	15	190	1.67×10^{-3}	4	155	48
26	40	231	1.67×10^{-3}	1	24	–
16	82.5	301	1.67×10^{-3}	5	11	7

followed by determination of the Cl^- content by ion chromatography. Under the conditions used, the HCl in the bubbler water remained very unsaturated relative to the gas phase (Fritz and Fuget, 1956), so that all the HCl was effectively trapped in the bubbler. The crystallization tube had an internal diameter of 5 cm and the gas mixture flowed into it at a rate of 1.5 L/minute through a glass sphere 1.5 cm in diameter (Fig. 1) where 20 holes had been made to maximize turbulent mixing in the tube. The temperature of the ball was not measured. Its value was the result of heat exchanges between the warm incoming gases and the cold reactor walls. Since experiments at supersaturations of 82.5% did not result in ice formation on the ball, we deduce that its temperature was $>-8.4^{\circ}\text{C}$. The pressure in the crystallization tube was about 960 mbar. The ice growing on the tube inner surface formed small (<0.5 mm) crystals whose detailed morphology could not be observed at the bottom of the tube. The ice stopped growing abruptly at the level of immersion of the tube, and appeared to form a layer of homogeneous thickness where it grew. The maximum mass of ice that could form was predicted from the supersaturation and the gas flow rate, and this was equal to the measured mass of ice, within 15%. Two methods were used to retrieve the solid solution of HCl in ice formed: melting in the tube followed by analysis, and scraping of the inside of the tube in a cold room at -15°C followed by analysis by ion chromatography using a Dionex 4000i instrument located in a clean room. Both methods produced similar results. Numerous tests and blanks were performed to identify and minimize possible sources of contamination.

Eight blank runs with no HCl were performed under flow conditions similar to the experiments with HCl. Cl^- concentrations in the ice of these blanks ranged from 2 to 9 10^{-9} mole fraction (hereafter ppb) with an average of 5 ppb. Cl^- was below detection limit (0.5 ppb) in the water poured into the bubblers, and the source of the contamination was not clearly identified. Tests showed the N_2 , obtained from evaporating liquid N_2 , to be very clean. We rather believe that it is caused by HCl released from tubing or from flowmeters, that are difficult to clean perfectly, as HCl readily sticks to surfaces. In any case, the blank values were significantly

**Fig. 2.** Molar fraction of HCl (detected as Cl^- by ion chromatography) in ice as a function of the supersaturation of the gas mixture relative to ice at -15°C . Error bars are the standard deviations when several experiments were made (see Table 1). The experimental data are compared to the predictions of Eq. (4), using values of A , h , D_{gas} , X_{kin} and X_{eq} detailed in the text.

lower than the signal, and were simply subtracted from the experimental values.

Before each experiment, the gas lines and the crystallization tube were conditioned by flowing the experimental mixture through them at room temperature for at least one hour.

3 Results and discussion

Since our objective was to study the impact of the ice growth rate on HCl incorporation, 10 experiments were performed by varying the water supersaturation, and hence the ice growth rates, while maintaining total flow, temperature, and P_{HCl} constant. Results obtained at $T = -15^{\circ}\text{C}$, for $P_{\text{HCl}} = 1.67 \times 10^{-3}$ Pa are shown in Table 1 for supersaturations of 15, 40, and 82.5%. Under those conditions, the equilibrium HCl mole fraction in ice is $X_{\text{eq}} = 3120$ ppb (Thibert and Domine, 1997). The values obtained after subtracting blank values are between 11 and 155 ppb, much lower than X_{eq} , indicating that kinetic processes play an important role

in determining X_{HCl} . Figure 2 shows a plot of the 3 values of X_{HCl} as a function of supersaturation.

These data were used to test the validity of Eq. (3) and to determine the value of h , the height of the ice growth step. To compare our experimental data to this equation, we need to express X_{gas} as a function of the water vapor supersaturation, S . We assume here that the linear growth rate of the ice, v , is proportional to S , so that $v=A \times S$. The growth rate v and h are related by $\tau=h/v$, so that $\tau=h/AS$, and Eq. (3) can be written as :

$$X_{\text{gas}} = X_{\text{kin}} + \frac{(X_{\text{eq}} - X_{\text{kin}})}{h} \int_0^h \text{erfc} \left(x \sqrt{AS/2\sqrt{D_{\text{gas}}h}} \right) dx \quad (4)$$

which relates X_{gas} to S . To plot Eq. (4), we need to evaluate A , D_{gas} and h . The growth rate can be inferred from the mass of ice that was retrieved and the surface area over which it grew. For the experiments at 15% supersaturation, the growth rate found was about $1 \mu\text{m/s}$, from which we deduce that $A=6.7 \times 10^{-6} \mu\text{m s}^{-1}$. At -15°C , the diffusion coefficient of HCl in ice is about $2 \times 10^{-12} \text{cm}^2/\text{s}$ (Thibert and Domine, 1997). Other values have been proposed for this parameter, but Thibert and Domine (1997) and subsequently Domine and Xueref (2001) have explained in detail why those other values are highly questionable. The height of the growth step, h , was determined by solving numerically Eq. (3) using the data at 15% supersaturation, and also by optimizing the agreement between the curve and the experimental data. A value of $h=150 \text{nm}$ was obtained using either method, and the resulting curve is shown in Fig. 2, where the agreement with the data is good, given the experimental uncertainty. In this curve, a value of $X_{\text{kin}}=11 \text{ppb}$ was used. A somewhat lower value may slightly improve the fit, but not in a meaningful manner given the experimental uncertainties. Equation (4) indicates that the supersaturation required to approach equilibrium is around 0.1%, which is not achievable in our experimental setup, as growth would be much too slow.

The value of h that we deduce here is of the same order of magnitude as that found by Hallett (1961), who grew ice crystals on covellite surfaces and measured h values of 20 to 100 nm. However, most of these early studies focused on the basal face, while at our experimental temperature of -15°C , growth takes place on the prism face. In any case, crystal growth parameters are influenced by numerous variables such as growth rate, the nature of the surface on which crystals are grown, the crystallographic face and the defect density, so that there is little reason why values of h found in one study should be reproduced in another study using different experimental conditions.

Equation (3) was derived to have a general validity. At fast growth rates, such as obtained for a supersaturation of 82.5%, it simplifies to Eq. (1), which can then be used to estimate $\gamma_{\text{HCl}}/\gamma_{\text{H}_2\text{O}}$ on ice. We obtain a value of 0.0028. We note that this value is very different from what would be expected

if surface processes only were operative, and mass accommodation coefficients α could be used to predict X_{kin} . The parameter α_{HCl} has been measured in the laboratory around -80°C , and values between 0.1 and 1 have been found (Leu et al., 1988; Hanson and Ravishankara, 1992). Similarly, $\alpha_{\text{H}_2\text{O}}$ is in the range 0.1 to 1 (Haynes et al., 1992 and references therein), so that $\alpha_{\text{HCl}}/\alpha_{\text{H}_2\text{O}}$ is expected to be in the range 0.1 to 10. If surface processes only determine HCl uptake, $\gamma_{\text{HCl}}/\gamma_{\text{H}_2\text{O}}$ would then be expected to be between 10 and 0.1. Why the HCl content of our ice samples is so low at fast growth rates deserves discussion.

The first thought is that gas phase diffusion may be limiting. To a first approximation, this process should affect both HCl and H_2O because $\alpha_{\text{H}_2\text{O}}$ and α_{HCl} are of the same order of magnitude. However, essentially all of the excess H_2O condensed in our tube, indicating that gas phase diffusion limitations in this turbulent reactor did not affect H_2O . We thus do not expect diffusion to limit HCl uptake either. Moreover, the fraction of HCl transferred from the gas phase to the ice phase is smaller than that of H_2O . Indeed, $P_{\text{HCl}}/P_{\text{H}_2\text{O}}$ is always around 10^{-5} , while X_{HCl} is about 10^{-8} in this fast growth experiment, so that gaseous HCl will be much less depleted than H_2O in the vicinity of the ice surface. Since we observed that the loss of HCl is much smaller than that of H_2O , HCl is necessarily less affected by diffusion limitations than H_2O , and this process probably cannot explain our low γ ratio. Desorption of HCl must then be responsible for the low γ ratio.

To evaluate quantitatively this desorption, a budget of HCl at the ice surface must be established. This cannot be done, because we only have an approximate value of α_{HCl} . However, in the fast growth experiment, the mole fraction of HCl in the gas phase is about 5×10^{-6} , while it is about 10^{-8} in the solid phase. If $\alpha_{\text{H}_2\text{O}}$ and α_{HCl} were equal, this would mean that 99.8% of the HCl that initially adsorbs subsequently desorbs before being incorporated in ice.

Santachiara et al. (1995) also studied the incorporation of HCl in ice crystals growing by the Bergeron mechanism from water droplets containing HCl in a diffusion chamber at -13°C . They found X_{HCl} values up to 3000 ppm, much higher than the maximum thermodynamic solubility (Thibert and Domine, 1997). However, they induced ice nucleation by introducing “a small metal bar cooled in liquid nitrogen” in their chamber, creating a cold spot. It then seems that neither the crystal growth temperature, nor P_{HCl} can be determined, and it is not possible to compare their results with ours.

Diehl et al. (1995) grew ice crystals from water vapor at -15°C , with a supersaturation estimated at about 15% in a diffusion chamber, and in the presence of HCl. Their lowest P_{HCl} was about $5 \times 10^{-3} \text{Pa}$, and the resulting X_{HCl} was about 200 ppb. Besides P_{HCl} , their conditions are similar to our experiments at 15% supersaturation, and we found 155 ppb under $P_{\text{HCl}}=1.67 \times 10^{-3} \text{Pa}$. If we compare their results to ours according to Eq. (1), i.e. assuming that kinetic processes rule incorporation, then their concentration is a factor of 2.3

lower than expected from our results. On the other hand, if the comparison is done using Eq. (2), i.e. using a $P_{\text{HCl}}^{\frac{1}{2.73}}$ dependence, then their result should be 1.5 times greater than ours, i.e. 232 ppb, definitely within the overlap of their error bars and ours. Since Diehl et al. (1995) used a set up very different from ours that could result in a different value of h , and since according to Eq. (3) the value of h greatly influences X_{HCl} , we conclude that the X_{HCl} value of Diehl et al. is compatible with ours. However, their purpose was not to test the impact of the growth rate on HCl incorporation, and their data can thus not be used to test our mechanism.

The variability of crystal growth parameters such as h , but also $\alpha_{\text{H}_2\text{O}}$ and α_{HCl} , with experimental conditions thus makes it difficult to intercompare experiments. The application of laboratory data to natural conditions is even more delicate and deserves a separate discussion.

4 Application to snowpacks and clouds

The main conclusion of this work is that the experimental data obtained is consistent with the mechanism of Domine and Thibert (1996), which showed that the composition of ice depends on its growth rate and on the details of its growth mechanism. Given that we have argued that the variables that determine the growth of snow crystals, and hence the incorporation of trace gases, vary between different laboratory experiments, and presumably between the different conditions encountered in clouds and in snowpacks, quantitative application of this mechanism to the natural environment appears impossible until we understand the details of ice crystal growth in nature, and we seem to be very far from this goal. Domine et al. (2003) may have observed growth steps on surface hoar crystals studied by scanning electron microscopy (SEM), and whose height was about $1\text{ }\mu\text{m}$, but it is not even totally certain that the structures observed were growth steps, and they did not seem to originate from a crystal edge, but rather from a grain boundary, so that the representativity of this observation may be limited. Indeed, the numerous SEM studies of snow crystals (Wergin et al., 1996; Domine et al., 2003; Erbe et al., 2003; Legagneux et al., 2003) usually do not show any structures that can be convincingly attributed to growth steps, which suggest that these could be undetectable by SEM and much smaller than $1\text{ }\mu\text{m}$ in most cases.

Furthermore, in nature, the ice surface and the adsorption of trace gases can be modified by the presence of numerous pollutants. For example Hynes et al. (2002) have observed that adsorbed HCl was displaced from the ice surface in the presence of HNO_3 . The ubiquitous sulphate aerosols can also be scavenged by ice surfaces and form a liquid or disordered film that could dramatically modify ice surfaces and the incorporation of trace gases, as the first step in incorporation is adsorption.

Given our limited understanding of the growth of snow crystals in nature, we are limited to speculate qualitatively

on the interactions between crystal growth rate and chemical composition. For species highly soluble in ice such as HCl, $X_{\text{kin}} < X_{\text{eq}}$ under most atmospheric conditions and faster growth rates will lead to lower concentrations. Thus, the small columnar ice crystals that form slowly in cirrus clouds at low temperature should be more concentrated in Cl^- than the larger dendritic crystals that grow rapidly in the warmer stratiform clouds. In the snowpack, the rapidly growing depth hoar crystals should be depleted in Cl^- relative to windpack crystals, that grow much more slowly. This should be true at least in acidic snow, where the Cl^- measured by ion chromatography indeed reflects HCl content, while it would have little reason to hold in alkaline snow, where the Cl^- signal reflects the content of particulate Cl^- , present in snow as salts such as NaCl. Field measurements of different snow crystal types in a given snow pack would be a feasible test of this prediction.

The situation is probably different for HNO_3 , which is about 20 times less soluble in ice than HCl (Thibert and Domine, 1998). In this case, the data available suggest that at high temperature, we still have $X_{\text{kin}} < X_{\text{eq}}$, but at low temperature, we should have $X_{\text{kin}} > X_{\text{eq}}$. The limit between “high” and “low” temperature will depend on the physics of ice crystal growth, and particularly on h . In the Arctic or subarctic snowpack, since depth hoar crystals are at the relatively warm bottom part of the snowpack while windpacks are at the colder top part (Domine et al., 2002), we have all reasons to expect a higher NO_3^- concentration in the windpack, and again this prediction applies only to acidic snow.

5 Conclusions

The experiments performed here are consistent with the predictions of the mechanism of Domine and Thibert (1996) that proposed an interaction between the growth rate of ice crystals and their chemical composition. The nature of the crystallographic face, the nucleation mechanism and step height, h , of new ice layers, and other variables describing the state of the growing ice surface will influence ice composition. The immediate implication is that considerable efforts must be devoted to the physics of ice crystal growth under natural conditions if we want to understand the composition of ice crystals in clouds and in the snowpack.

It is also noteworthy that this mechanism does not need to invoke the much talked about “quasi-liquid layer” (QLL) on the ice surface. It is certain that this QLL does exist, as it has been evidenced by numerous techniques (Petrenko and Witworth, 1999), including a recent study by atomic force microscopy (Döppenschmidt and Butt, 2000) that concluded that its thickness at -15°C was between 5 and 10 nm. Several authors (e.g. Valdez et al., 1989; Conklin and Bales, 1993) have interpreted gas uptake by growing ice in terms of solubilization of the gas in the QLL, using thermodynamic parameters of actual liquid water. But the QLL properties

are definitely different from those of liquid water, and using parameters measured for liquid water is unwarranted. Moreover, the model used by those authors led them to conclude that the QLL thickness in pure ice was greater than 100 nm at -15°C , in sharp contrast with the actual measurements of Döppenschmidt and Butt (2000). Further supporting the idea that the QLL need not be invoked to explain ice growth at -15°C , many physical properties of ice growth have been explained successfully by considering solid state processes only (Libbrecht, 2003a and b; Nelson and Baker, 2003; Nelson, 1998; Nelson and Knight, 1998).

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